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(21) 出願番号	特願平11-35634	(71) 出願人	000229117 日本ゼオン株式会社 東京都千代田区丸の内2丁目6番1号
(22) 出願日	平成11年2月15日 (1999. 2. 15)	(72) 発明者	八木 宏 神奈川県川崎市川崎区夜光一丁目2番1号 日本ゼオン株式会社総合開発センター内
		(72) 発明者	松村 博行 神奈川県川崎市川崎区夜光一丁目2番1号 日本ゼオン株式会社総合開発センター内
		(72) 発明者	上和野 満雄 神奈川県横浜市旭区中尾一丁目33番13号
		(74) 代理人	100097180 弁理士 前田 均 (外1名)

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(54) 【発明の名称】 攪拌翼及びこれを用いた攪拌装置

(57) 【要約】

【課題】 比較的高粘度の液体であっても、少ない電力量で効率的かつ均一に混合することができる攪拌翼及びこれを用いた攪拌装置を提供する。

【解決手段】 攪拌軸を介して駆動手段により回転駆動され、一定幅の帯状板が螺旋面を成すように形成されたヘリカルリボン翼を有する攪拌翼であって、前記帯状板に該帯状板の外側端部より突出するような突起部を設けてある攪拌翼、及び攪拌槽と該攪拌槽内に同芯状に設けられる前記攪拌翼とを少なくとも有する攪拌装置である。

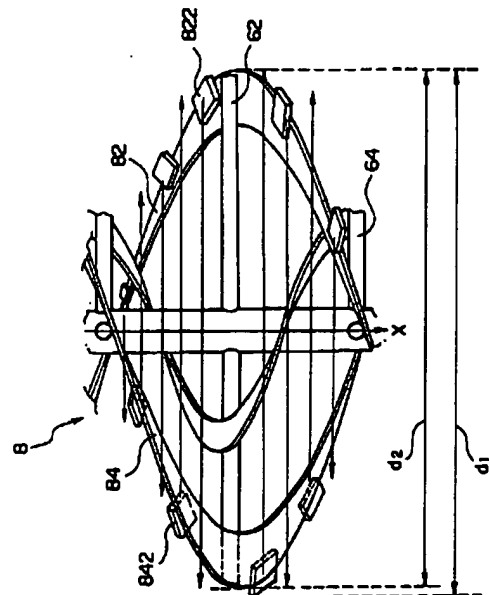


図 2

【特許請求の範囲】

【請求項1】 攪拌軸を介して駆動手段により回転駆動され、一定幅の帯状板が螺旋面を成すように形成されたヘリカルリボン翼を有する攪拌翼であって、

前記帯状板に、該帯状板の外側端部より突出する突起部を設けてあることを特徴とする攪拌翼。

【請求項2】 少なくとも2条のヘリカルリボン翼を有し、前記攪拌軸を中心線として線対称となる一方の帯状板上に設けてある突起部と、他方の帯状板上に設けてある突起部とが、中心線に対する同一垂直面で同じ位置に存在しないよう交互に配置してあることを特徴とする請求項1記載の攪拌翼。

【請求項3】 前記ヘリカルリボン翼の最終端同士を連結部材で連結してあることを特徴とする請求項2記載の攪拌翼。

【請求項4】 攪拌槽と、該攪拌槽内に同芯状に設けられる請求項1～3の何れかに記載の攪拌翼とを少なくとも有することを特徴とする攪拌装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、特に、比較的高粘度の液体であっても、少ない電力量で効率的かつ均一に混合することができる攪拌翼及びこれを用いた攪拌装置に関する。

【0002】

【従来の技術】例えば、溶液中でポリマーの重合を行う溶液重合は、通常、重合効率の向上を図るため攪拌装置内にモノマーと溶媒を投入後攪拌しながら行われる。また、溶液重合は、モノマー濃度を変化させることが比較的容易であり、ポリマーの生産性を向上させるために初期添加するモノマー濃度をより多くすることが望まれる。しかしながら、モノマー濃度が多くなれば溶液粘度がそれだけ高くなり、必然的に攪拌作業効率が低下することとなる。

【0003】従来、この種の攪拌装置としては、その外径が攪拌槽の内径よりも十分に小さいヘリカルリボン状の攪拌翼を備えたものが知られている。しかしながら、こうした攪拌装置を用いて比較的高粘度の液体を混合すると、攪拌槽と攪拌翼との間隙部分で液が停滞してしまい、槽内全体での液の均一な混合が妨げられていた。

【0004】これに対し、攪拌翼の外径を大きくし、即ち、攪拌槽内壁面と攪拌翼との間隙を少なくすることにより該間隙部分における液の停滞を防止することが考えられる。しかしながら、これでは、攪拌翼の駆動負担が大きくなり、従って該攪拌翼駆動装置の出力を上げる必要があり、攪拌装置の省電力化が図れなくなる。

【0005】

【発明が解決しようとする課題】本発明は、このような従来技術の問題点に鑑みなされたものであり、比較的高

粘度の液体であっても、少ない電力量で効率的かつ均一に混合することができる攪拌翼及びこれを用いた攪拌装置を提供することを目的とする。

【0006】

【課題を解決するための手段】上記目的を達成するために、本発明に係る「攪拌翼」は、攪拌軸を介して駆動手段により回転駆動され、一定幅の帯状板が螺旋面を成すように形成されたヘリカルリボン翼を有する攪拌翼であって、前記帯状板に、該帯状板の外側端部より突出する突起部を設けてあることを特徴とする。

【0007】本発明において、前記帯状板に設けてある突起部は、少なくとも帯状板の外側端部より突出していればよく、例えば、帯状板の表裏面の少なくとも何れかの面に外側端部に突出するように設ける、帯状板の外側端部に設ける等が考えられる。またこの突起部の形成方法も別段特に限定されず、前記帯状板を成形する際に一体成形しても、又は、一旦、帯状板と突起部を別々に成形し、その後帯状板に突起部を後付けすることとしてもよい。後付けする手段としては特に限定されず、例えば溶接、接着、ボルト・ナットによる連結等が例示される。

【0008】本発明において、突起部を持つヘリカルリボン翼の数は特に限定されないが、好ましくは少なくとも2条有することが望ましく、より好ましくは少なくとも2条のヘリカルリボン翼を有し、前記攪拌軸を中心線として線対称となる一方の帯状板上に設けてある突起部と、他方の帯状板上に設けてある突起部とが、中心線に対する同一垂直面で同じ位置に存在しないよう交互に配置してあることが望ましい。

【0009】本発明において、突起部を持つヘリカルリボン翼の数が3条以上有する場合は、攪拌軸の軸方向に対して垂直方向から攪拌翼を見た場合において、同じ高さ位置に相当する帯状板上には何れか一の帯状板上にのみ突起部を設け、他の帯状板上には突起部を設けないように前記突起部を順次設けることが望ましい。

【0010】本発明において、前記ヘリカルリボン翼を有する攪拌翼の突起部を含む外径 $d_1$ と、攪拌槽の内径 $D$ との関係は、 $(d_1/D) = 0.85$ 以上1未満、好ましくは $0.93$ 以上 $0.97$ 以下であることが望ましい。また攪拌翼の突起部を含む外径 $d_1$ と、突起部を含まない外径 $d_2$ と、攪拌槽の内径 $D$ との三者の関係は、 $((d_1 - d_2)/D) = 0.001$ 以上 $0.5$ 以下、好ましくは $0.03$ 以上 $0.25$ 以下、より好ましくは $0.10$ 以上 $0.15$ 以下であることが望ましい。

【0011】本発明において、前記ヘリカルリボン翼の最終端同士を連結部材で連結してあることが望ましい。

【0012】本発明に係る「攪拌装置」は、攪拌槽と、該攪拌槽内に同芯状に設けられる前記何れかの攪拌翼とを少なくとも有することを特徴とする。

【0013】

【作用】駆動装置の駆動負担を考えると、攪拌翼を攪拌槽内に同芯状に設ける場合、ヘリカルリボン翼を構成する帯状板の外径と攪拌槽の内径との間の間隙は大きい程良い。しかし、従来の攪拌翼では攪拌翼駆動装置に過大な負担をかけない程度に間隙幅を設けると、該間隙部で攪拌・混合されるべき液が停滞してしまい、その結果、槽内全体での液の均一な混合が妨げられていた。本発明によれば、帯状板の外側端部より突出するような突起部を帯状板に設けてあるので、駆動装置に負担をかけることなく、間隙部分での液の掻き取りを効率的に行え、従って、槽全体として少ない電力で効率的かつ均一な混合が可能となる。また、攪拌軸の軸方向に対して垂直方向から攪拌翼を見た場合において、同じ高さ位置に相当する帯状板上の一方に突起部を有する場合には他方には突起部を有しないように前記突起部を順次交互に設けることにより、攪拌軸の回転駆動中に一方の突起部で掻き取れない部分を他方の突起部で効率的に掻き取ることができ、攪拌効率のさらなる向上が図れる。

【0014】

【発明の実施の形態】以下、本発明の実施形態につき図面を参照しながら説明する。

#### 第1実施形態

図1は本発明の第1実施形態に係る攪拌翼を用いた攪拌装置の概要を示す図、図2は図1における符号IIの部分拡大図、図3は図2における突起部付近の部分平面図である。

【0015】図1に示すように、本実施形態に係る攪拌装置2は、攪拌槽4、攪拌軸6及び攪拌翼8を有する。攪拌槽4は、円筒胴42と、この円筒胴42の下端部に配置された半円形断面形状を持つ底板44とを有し、前記円筒胴42が略垂直方向に配置してある。なお、図示省略してあるが、攪拌時には前記円筒胴42の上端部に上蓋が取り付けられる。またこの攪拌槽4は、例えば金属やガラス等で構成される。

【0016】攪拌軸6は、円筒胴42と同芯状の攪拌槽4の内部に回転駆動自在に配設してある。なお、この攪拌軸6を回転駆動させるために、その上端部が図示省略してあるモーター装置等の駆動手段に連結される。また、攪拌軸6には、所定の間隔を置いて水平に複数突設された腕木62及び64が形成してある。なお、この攪拌軸6は、例えば金属等で構成される。

【0017】本発明の攪拌翼は、攪拌槽の形状（縦型槽、横型槽など）に応じて任意の設置をすることができ、図1では、縦型槽に対して縦に配置しているが、横型槽では横に設置してもよい。

【0018】本実施形態において、腕木62の両端部には2条のヘリカルリボン翼（以下、ダブルヘリカルリボン翼ともいう）82及び84が取り付けられており、腕木62の途中及び腕木64の端部には1条のヘリカルリボン翼（以下、シングルリボン翼ともいう）86が取り付けられている。

これらの両ヘリカルリボン翼82、84及び86は、それぞれ、一定幅の帯状板が螺旋面を成すよう形成してあり、これらを合わせることで本実施形態における攪拌翼8を構成する。

【0019】また、本実施形態においてはダブルヘリカルリボン翼82及び84と、シングルリボン翼86との外径を異ならせている。異なる外径を持つ複数のヘリカルリボン翼とすることにより攪拌槽4の内外部いずれの部分においても均一な混合が達成可能となる。なお、本実施形態においてはシングルリボン翼86を設けているが、本発明では必ずしも設ける必要はない。

【0020】また、図2に示すように、本実施形態におけるダブルヘリカルリボン翼82及び84は、リボン翼を構成する帯状板の表面から該帯状板の外側端部より突出するような突起部822及び842が設けてある。この突起部は、その取り付け方や配置方法によって特に限定されない。例えば図2及び図3に示すように、突起部822として正方形の板を用いた場合には、帯状板の外周が正方形の中心を通過するよう配置される。なお、この突起部822及び842の形状は、正方形には特に限定されず、三角形、菱形、五角形以上の多角形等も使用可能である。また、リボン翼を構成する帯状板上に設けられる複数の突起部は、その大きさ、形、が同じである必要はなく、不揃いの大きさ、形のものであってもよい。また、隣接する突起部同士の間隔も特に限定されず、等間隔であっても不等間隔であってもよいが、実施形態として等間隔になるよう配置することが好ましく、より好ましくは攪拌軸6の軸方向から見て帯状板の螺旋面180°ごとにつき突起部を約4～約8個設け、これらを等間隔に配置することが望ましい。こうした配置により突起部を設けることにより効率的な混合が一層可能となる。なお、本実施形態における攪拌翼8の帯状板82及び84、並びに突起部822及び842の材質は特に限定されず、例えば金属等で構成される。また本実施形態では、既存の攪拌翼8の帯状板82及び84に、突起部822及び842をボルト・ナット等で固定してある。

【0021】また、本実施形態では、攪拌軸6を中心線として線対称となる一方の帯状板82上に設けてある突起部822と、他方の帯状板84上に設けてある突起部842とが、中心線に対する同一垂直面で同じ位置に存在しないよう交互に配置してあることが望ましい。即ち、図2に示すように、攪拌軸6の軸方向（図2中のX方向）に対して垂直方向から攪拌翼8を見た場合において、同じ高さ位置に相当する帯状板82及び84上の一方（例えば、帯状板82）に突起部を有する場合（例えば、図2中の符号822の突起部に相当する）には他方（例えば帯状板84）には突起部を有しないように前記突起部を設ける（例えば、図2中の符号842の突起部に相当する）ことで、攪拌軸6の回転駆動中に一方の突

起部で掻き取れない部分を他方の突起部で効率的に掻き取ることができ、攪拌効率のさらなる向上が図れる。なお、本実施形態では、突起部822と突起部842とが、同一垂直面で同じ位置に存在しないように配置してあるが、本発明では必ずしもこれに限定されず、突起部822と突起部842の同一垂直面における位置が、多少、重なりあってもよい。

【0022】本実施形態においてダブルヘリカルリボン翼82及び84の突起部を含む外径d1は、図2に示すように、攪拌槽4の内壁に接触しないよう、攪拌槽4の内径Dを1とした場合に、0.85以上1未満の範囲で適宜決定される。即ち通常はリボン翼82及び84の突起部を含んだ形での外径と攪拌槽4の内壁との間に間隙幅 $((D-d1)/2)$ が形成される。またリボン翼82及び84の突起部を含む外径d1と、突起部を含まない外径d2（リボン翼82及び84の外径）と、攪拌槽4の内径Dとの三者の関係は、 $((d1-d2)/D) = 0.001$ 以上0.5以下の範囲で適宜決定される。

【0023】なお、本実施形態では突起部822及び842を持つヘリカルリボン攪拌翼の数を2条としてあるが、別段これに限定する趣旨ではなく、3条以上であってもよい。突起部を持つヘリカルリボン翼の数が3条以上有する場合は、攪拌軸6の軸方向に対して垂直方向から攪拌翼8を見た場合において、同じ高さ位置に相当する帯状板上には何れかの帯状板上にのみ突起部（図示省略）を設け、他の帯状板上には突起部（図示省略）を設けないように前記突起部を設けることで、同様の効果を得ることができる。

【0024】以上の構成の攪拌装置2の攪拌槽4内に、比較的高粘度の液体を内容液として投入し該内容液の攪拌・混合を行う。

【0025】次に、本実施形態に係る攪拌装置2の作用を説明する。図1に示す攪拌槽4内に内容液を投入した後、図示省略してある駆動手段を始動して、内容液の流れが攪拌槽4の中心部で上向き（矢印B方向）になるように攪拌軸6を回転駆動させると（矢印A方向）、攪拌槽4の円筒胴42内で回転するダブルヘリカルリボン翼82、84及びシングルリボン翼86が、内容液を下方かつ外周側から底板に沿って攪拌軸6側へと内容液を送り込む。そして、ヘリカルリボン翼によって攪拌軸6に沿って上方（矢印B方向）に液送りされた後、液表面近くでその流れが外周側に変換され、さらには攪拌槽4の円筒胴に沿って下向き（矢印C方向）に下降し、底板近くで攪拌軸6側に送られる。ここで、本実施形態では、ダブルヘリカルリボン翼82及び84を構成する帯状板の外側端部より突出するような突起部をそれぞれの帯状板に特定の配置で設けてあるので、駆動装置に負担をかけることなく、間隙部分 $((D-d1)/2)$ での液の掻き取りを効率的に行え、混合不良を生じるおそれが少ない。このような一連のフローパターンにより、少

ない電力量で均一に高粘度液体を攪拌・混合することができるようになる。

#### 【0026】第2実施形態

図4は本発明の他の実施形態に係る攪拌翼を示す図である。

【0027】本実施形態に係る攪拌装置は、図1に示す攪拌翼6のボトム部が、前記第1実施形態に係る攪拌装置と異なるのみであり、以下に示す説明では、相違点についてのみ特に詳細に説明し、共通する部分の説明は省略する。

【0028】図4に示すように、本実施形態に係る攪拌装置2は、攪拌翼8を構成するダブルヘリカルリボン翼82及び84のそれぞれのボトム部分（最終端）を連結部材10で連結してある。攪拌翼中に不連続部分があると、特に混合する液粘度が高くなればなるほど流れの伝わり方が悪化する傾向にあり、本実施形態におけるようにダブルヘリカルリボン翼82及び84のボトム部分を連結することにより、攪拌中における液の流れの伝わり方を好適に保持することができ、従って一層の攪拌性能の向上が期待できる。

#### 【0029】その他の実施形態

なお、本発明は、上述した実施形態に限定されず、本発明の範囲内で種々に改変が可能である。例えば、上述の実施形態では攪拌槽4の底板44の断面形状を半楕円形としたが、別段これに限定されず、その他皿形や鈍角頂角を有する円錐形としてもよい。

#### 【0030】

【実施例】以下の実施例に基づき本発明をさらに詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

#### 【0031】実施例1

攪拌装置として、図1～3に示す装置を用いた。攪拌槽4としては、260mmの内径及び260mmの高さを持つ円筒胴42に、65mmの深さを持つ半楕円形の底板44を取り付けたガラス製透明攪拌槽を使用した。攪拌翼8としては、212mmの外径を持つダブルヘリカルリボン翼82及び84と、106mmの外径を持つシングルリボン翼86とが、攪拌軸6に所定の間隔を置いて水平に複数突設された腕木62及び64の両端部に接続された攪拌翼8を使用した。またダブルヘリカルリボン翼82及び84を構成する帯状板の表面には、該帯状板の外側端部より15mm突出するような縦30mm×横30mmの正方形の板からなる突起部822及び842を、攪拌軸6の軸方向から見て帯状板の螺旋面180°ごとにつき突起部が5個等間隔になるよう設けた。ダブルヘリカルリボン翼82及び84の突起部を含む外径d1と、攪拌槽4の内径Dとの関係は、 $(d1/D) = 0.93$ であり、攪拌槽4の内壁面と攪拌翼8との間隙幅 $((D-d1)/2)$ は9mmであった。なお、攪拌装置2を、攪拌軸6の軸方向（図2中のX方向）に対し

て垂直方向から攪拌翼8を見た場合において、同じ高さ位置に相当する帯状板上の一方に突起部を有する場合

(例えば、図2中の符号822の突起部に相当する)には他方には突起部を有しないように前記突起部を設けた(例えば、図2中の符号842の突起部に相当する)。またダブルヘリカルリボン翼82及び84のそれぞれのボトム部分を幅26mmの金属製連結部材で連結した。なお、攪拌翼8の帯状板及び突起部の材質はともに金属であり、連結部材の材質も金属であった。以上の構成の攪拌装置の概要を図5に示す(但し、図5では突起部及び連結部材は図示省略してある)。

【0032】この攪拌装置を用いて、38,000cPの粘度を持つカルボキシメチルセルロースナトリウム塩水溶液(以下、単に、「CMC水溶液」ということがある。)液16.1リットルを攪拌槽内へ投入して攪拌動力の測定を行った(動力測定の評価)。攪拌動力の測定は、攪拌軸の回転数を50～100rpmの間隔で上げていき、トルクメーターにより測定した。そして、攪拌翼の攪拌動力(Pv)が1.5kW/m<sup>3</sup>のとき、及び3.0kW/m<sup>3</sup>のとき双方の攪拌翼の回転数を算出した。前者のときは65rpm、後者のときは105rpmであった。なお、攪拌動力は、予め同一回転数で無負荷運転の動力を測定値より差し引いて攪拌動力とした。次に、58,800cPの粘度を持つCMC水溶液16.1リットルの攪拌動力の測定を、38,000cPの場合と同様に行った。攪拌動力が1.5kW/m<sup>3</sup>のときは56rpm、3.0kW/m<sup>3</sup>のときは93rpmであった。これらの攪拌動力の測定結果を表1に示す。

【0033】また、同様の攪拌装置を用いて、38,000cPの粘度を持つCMC水溶液16.1リットルを攪拌槽内に投入し、でんぷん10%水溶液を50cm<sup>3</sup>を添加して、均一になるまで混合し、次いでヨウ素が6%及びヨウ化カリウムが17%の濃度となる混合水溶液3cm<sup>3</sup>を加えてCMC水溶液を着色し、次いで、チオ硫酸ナトリウム20%水溶液を2cm<sup>3</sup>添加して攪拌を開始し、この着色の脱色が完了するまでの時間をストップウォッチにより測定した(混合性能の評価)。その結果、攪拌開始後70秒を経過すると着色部分がなくなり、完全に脱色された。次に、58,800cPの粘度を持つCMC水溶液16.1リットルを、38,000cPの場合と同様に着色後、混合性能の評価を同様に行った。その結果、攪拌開始後140秒を経過すると着色部分がなくなり、完全に脱色された。これら

の混合性能の評価の結果を表1に示す。

#### 【0034】実施例2

ダブルヘリカルリボン翼82及び84のそれぞれのボトム部分を連結部材で連結しなかった以外は実施例1と同様の攪拌装置を用い、実施例1と同様に攪拌動力の測定を行った。その結果、38,000cPの粘度を持つCMC水溶液における攪拌翼の攪拌動力が1.5kW/m<sup>3</sup>のときの回転数は66rpm、3.0kW/m<sup>3</sup>のときの回転数は107rpmであった。また、58,800cPの粘度を持つCMC水溶液における攪拌翼の攪拌動力が1.5kW/m<sup>3</sup>のときの回転数は57rpm、3.0kW/m<sup>3</sup>のときの回転数は95rpmであった。これらの攪拌動力の測定結果を表1に示す。

【0035】また、同様の攪拌装置を用いて、実施例1と同様の混合性能の評価を行った。その結果、38,000cPでは、攪拌開始後70秒を経過すると着色部分がほとんどなくなり、若干部分の着色を残しほぼ完全に脱色された。また、58,800cPでは、攪拌開始後140秒を経過すると着色部分がほとんどなくなり、若干部分の着色を残しほぼ完全に脱色された。これらの混合性能の評価の結果を表1に示す。

#### 【0036】比較例1

ダブルヘリカルリボン翼82及び84を構成する帯状板の表面に突起部を設けず、(d2/D)=0.819とした以外は実施例1と同様の攪拌装置を用い、実施例1と同様に攪拌動力の測定を行った。その結果、38,000cPの粘度を持つCMC水溶液における攪拌翼の攪拌動力が1.5kW/m<sup>3</sup>のときの回転数は84rpm、3.0kW/m<sup>3</sup>のときの回転数は137rpmであった。また、58,800cPの粘度を持つCMC水溶液における攪拌翼の攪拌動力が1.5kW/m<sup>3</sup>のときの回転数は70rpm、3.0kW/m<sup>3</sup>のときの回転数は114rpmであった。これらの攪拌動力の測定結果を表1に示す。また、同様の攪拌装置を用いて、実施例1と同様の混合性能の評価を行った。その結果、38,000cPでは、攪拌開始後70秒を経過しても、攪拌槽のボトム部に着色部分が残る、完全には脱色できなかった。また、58,800cPでは、攪拌開始後160秒を経過しても、攪拌槽の上部に大きな未消失部分が残るばかりか、この滞留部はその後の時間経過によっても消失しなかった。これらの混合性能の評価の結果を表1に示す。

#### 【0037】

#### 【表1】

表1

	動力測定(rpm)				混合性能(秒)	
	粘度(cp)				粘度(cp)	
	38,000		58,800		38,000	58,800
	撹拌動力(kw/m <sup>3</sup> )					
	3.0	1.5	3.0	1.5		
実施例 1	105 (77%)	65 (77%)	93 (82%)	56 (80%)	70秒で 完全脱色	140秒で 完全脱色
比較例 1	137	84	114	70	70秒後 も着色 あり	160秒後 かなりの 着色あり
実施例 2	107 (78%)	66 (79%)	95 (83%)	57 (81%)	70秒で ほぼ脱色	140秒で ほぼ脱色

【0038】考察      \*実施例1及び2中の( )内は、比較例1に対する実施例1の回転数(%)である。  
の効果が顕著に発揮される。

表1からも分かるように、本発明の撹拌翼を用いた場合には、10～20%程度の回転数低下が見られるが、混合効率は、回転数低下にもかかわらず、格段に向上している。具体的に、38,000cpのCMC水溶液において、比較例1では撹拌開始後70秒を経過しても、完全には脱色できなかったが、実施例1では撹拌開始後70秒を経過すると完全に脱色された(実施例2では70秒でほぼ完全に脱色された)。また、58,800cpのCMC水溶液において、比較例1では撹拌開始後160秒を経過しても、撹拌槽の上部に大きな未消失部分が残し、この滞留部はその後の時間経過によっても消失しなかったのに対し、実施例1では撹拌開始後140秒を経過すると着色部分がなくなり、完全に脱色された(実施例2では140秒でほぼ完全に脱色された)。このことから実施例1～2の撹拌装置の方が混合性能に優れていることが分かる。特に実施例1～2の撹拌装置は高粘度になればなるほどその優れた点が顕著になることが分かった。

【0039】

【発明の効果】以上説明してきたように、本発明によれば、比較的高粘度液体であっても、少ない電力量で効率的にかつ均一に撹拌・混合することが可能な撹拌翼及びこれを用いた撹拌装置が提供される。特に本発明の撹拌翼を用いた撹拌装置によれば、より高い粘度においてそ

【図面の簡単な説明】

【図1】図1は本発明の第1実施形態に係る撹拌翼を用いた撹拌装置の概要を示す図である。

【図2】図2は図1における符号IIの部分拡大図である。

【図3】図3は図2における突起部622付近の部分平面図である。

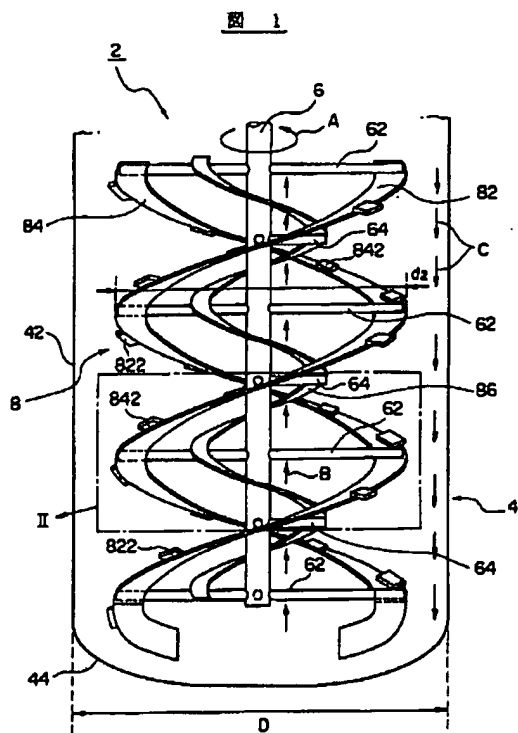
【図4】図4は本発明の他の実施形態に係る撹拌翼を示す図である。

【図5】図5は実施例で用いる撹拌装置の概要を示す図である。

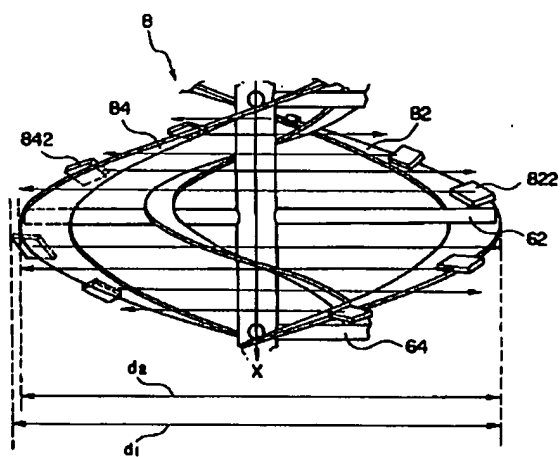
【符号の説明】

- 2… 撹拌装置
- 4… 撹拌槽
- 42… 円筒胴
- 44… 底板
- 6… 撹拌軸
- 62, 64… 腕木
- 8… 撹拌翼
- 82, 84… ダブルヘリカルリボン翼
- 822, 842… 突起部
- 86… シングルリボン翼
- 10… 連結部材

【图1】

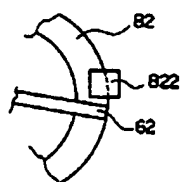


【图2】



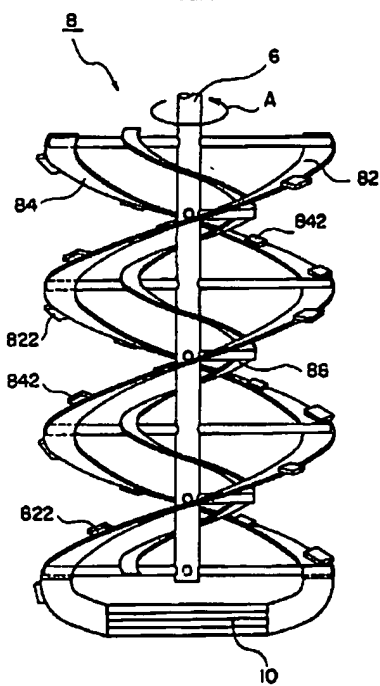
【图3】

图 3



【图4】

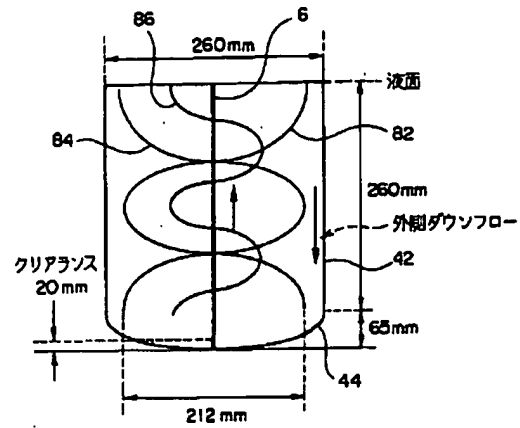
图 4





【図 5】

図 5



フロントページの続き

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POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY  
AND MANUFACTURING METHOD OF SAME, POSITIVE ELECTRODE FOR  
LITHIUM SECONDARY BATTERY MADE OF A POSITIVE ELECTRODE ACTIVE  
MATERIAL AND MANUFACTURING METHOD OF SAME, AND LITHIUM  
SECONDARY BATTERY MADE OF THE POSITIVE ELECTRODE AND  
MANUFACTURING METHOD OF SAME

[Richiumu nijiden'chiyoh seikyoku busshitsu oyobi sono seizoh houhoh, kono seikyoku  
busshitsuo mochiita richiumu nijiden'chiyoh seikyoku oyobi sono seizoh houhoh, kono  
seikyokuo mochiita richiumu nijiden'chi oyobi sono seizoh houhoh]

Inventor(s): Takuya Sunagawa  
c/o Sanyo Electric  
Co., Ltd.  
2-5-5 Keihan Hondori  
Moriguchi-shi  
Osaka-fu

[Inventors cont.] Hiroshi Watanabe  
c/o Sanyo Electric  
Co., Ltd.  
2-5-5 Keihan Hondori  
Moriguchi-shi  
Osaka-fu

Shin Fujitani  
c/o Sanyo Electric  
Co., Ltd.  
2-5-5 Keihan Hondori  
Moriguchi-shi  
Osaka-fu

Kohji Nishio  
c/o Sanyo Electric  
Co., Ltd.  
2-5-5 Keihan Hondori  
Moriguchi-shi  
Osaka-fu

Applicant(s): 000001889  
Sanyo Electric  
Co., Ltd.  
2-5-5 Keihan Hondori  
Moriguchi-shi  
Osaka-fu

Agent(s): 100064724  
Shoichi Hasegawa  
Patent attorney  
and 2 others

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*[There are no amendments to this patent.]*

*[Translator's note: The format of the source document supplied by the requester had been changed from the original Japanese Patent Application submitted by the applicant to accommodate machine translation.]*

**(54) [Title of the Invention]**

Positive electrode active material for lithium secondary battery and manufacturing method of same, positive electrode for lithium secondary battery made of the positive electrode active material and manufacturing method of same, and lithium secondary battery made of the positive electrode and manufacturing method of same

**(57) [Abstract]**

[Purpose] The purpose of the present invention is to produce a positive electrode active material with a reinforced crystal structure of lithium-nickel composite oxide so as to produce a positive electrode for lithium secondary battery and a lithium secondary battery with improved cycle characteristics and load characteristics.

[Means of solution] The positive electrode active material for lithium secondary battery of the present invention is provided with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$

(Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.45$  and  $0.5 \leq 1 - (b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees is in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[Claim of the invention]

[Claim 1] A positive electrode active material for lithium secondary battery containing a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which positive electrode active material for lithium secondary battery is characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.45$  and  $0.5 \leq 1 - (b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees is in the range of 0.15 degrees to 0.22 degrees when measurement is performed by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[Claim 2] A positive electrode active material for lithium secondary battery containing a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which positive electrode active material for lithium secondary battery is characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.40$  and  $0.5 \leq 1 - (b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees is in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[Claim 3] The positive electrode active material for lithium secondary battery described in

claim 1 or claim 2, in which the M in the aforementioned structural formula is Al.

[Claim 4] The positive electrode active material for lithium secondary battery described in one of claim 1 to claim 3, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, upon measurement by the aforementioned powder X-ray analysis of at least 0.8 is used selectively.

[Claim 5] A method of manufacturing a positive electrode active material for lithium secondary battery having a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which method of manufacturing a positive electrode active material for lithium secondary batteries is characterized by the fact that a substitution process where a portion of the nickel atoms of the lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included, and at the same time, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in the structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[Claim 6] A method of manufacturing a positive electrode active material for lithium secondary battery having a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which method of manufacturing a positive electrode active material for lithium secondary battery is characterized by the fact that the substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al,

Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included, and at the same time, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.40$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[Claim 7] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 5 or claim 6 characterized by the fact that a coprecipitation process in which the pH of the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a dissolved nickel compound, a dissolved manganese compound, and a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 8] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 5 or claim 6 characterized by the fact that an evaporation drying process, in which evaporation drying is performed for the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a dissolved nickel compound, a dissolved manganese compound and a dissolved M compound (wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is included.

[Claim 9] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 7 or claim 8, in which a heat-treatment process where a

mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.

[Claim 10] The manufacturing method of the positive electrode active material for lithium secondary battery described in one of claim 5 to claim 9 in which M in the aforementioned structural formula is Al.

[Claim 11] The method of manufacturing a positive electrode active material for lithium secondary battery described in one of claim 5 to claim 10, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is produced.

[Claim 12] In a positive electrode for lithium secondary battery containing a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a positive electrode for lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, is used as the aforementioned positive electrode active material, and at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material.

[Claim 13] In a positive electrode for lithium secondary battery containing a positive



electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a positive electrode for lithium secondary battery characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, is used as the aforementioned positive electrode active material, and at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material.

[Claim 14] The positive electrode for lithium secondary battery described in claim 12 or claim 13 in which the M in the aforementioned structural formula is Al.

[Claim 15] The positive electrode for lithium secondary battery described in one of claim 12 to claim 14, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta = 44.54 \pm 0.25$  degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is used selectively.

[Claim 16] A method of manufacturing a positive electrode for lithium secondary battery consisting of depositing a slurry comprised of at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder onto a current collector, which method of manufacturing a positive electrode for lithium secondary battery is characterized by the fact that a substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide

shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source and used as a positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector.

[Claim 17] A manufacturing method of a positive electrode for lithium secondary battery consisting of depositing a slurry comprising at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder onto a current collector, which method of manufacturing a positive electrode for lithium secondary battery is characterized by the fact that a substitution process where a portion of the nickel atoms of the lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese-M composite oxide shown in the structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.40$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, and it is used as a positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector.

[Claim 18] The method of manufacturing positive electrode for lithium secondary battery described in claim 17 or claim 18 characterized by the fact that the coprecipitation process, in which the pH of the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a

dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 19] The method of manufacturing a positive electrode for lithium secondary battery described in claim 17 or claim 18 characterized by the fact that the evaporation drying process, in which evaporation drying is performed for the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is included.

[Claim 20] The method of manufacturing the positive electrode for lithium secondary battery described in claim 18 or claim 19, in which a heat-treatment process where a mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide is performed to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.

[Claim 21] The method of manufacturing the positive electrode for lithium secondary battery described in one of claim 16 to claim 20, in which the M in the aforementioned structural formula is Al.

[Claim 22] The method of manufacturing the positive electrode for lithium secondary battery described in one of claim 16 to claim 22, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the

intensity of the peak observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta=44.54\pm0.25$  degrees (I2),  $I1/I2$ , upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is formed and used as the aforementioned positive electrode active material.

[Claim 23] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 24] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula

$\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.40$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 25] The lithium secondary battery described in claim 23 or claim 24, in which the M in the aforementioned structural formula is Al.

[Claim 26] The method of manufacturing the lithium secondary battery described in one of claim 23 to claim 25, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta = 44.54 \pm 0.25$  degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is formed and used as the aforementioned positive electrode active material.

[Claim 23] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-$

(b+c)≤0.95) and having the half-band width of the peak observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 27] In a manufacturing method of a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a method of manufacturing a lithium secondary battery characterized by the fact that the method includes the substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_1$ .

$_{(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1 - (b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where Cu-K $\alpha$  beam is used as the X-ray source and used as the aforementioned positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector to produce a

positive electrode, and furthermore, the positive electrode produced by the aforementioned positive electrode formation process is superimposed with a negative electrode capable of electrochemically storing and releasing the aforementioned lithium metal, lithium alloy, or lithium ion with the aforementioned separator in between and loaded to a battery tube and a nonaqueous solution is filled inside the aforementioned battery tube.

[Claim 28] A method of manufacturing a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, which method of manufacturing a lithium secondary battery is characterized by the fact that the method includes a substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is the above-mentioned element, and at the same time,  $0 < a \leq 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0.05 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source and used as the aforementioned positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector to produce the aforementioned positive electrode, and furthermore, the positive electrode produced by the aforementioned positive electrode formation process is superimposed with a negative electrode capable of electrochemically storing and releasing the aforementioned lithium metal, lithium alloy, or lithium ion with the aforementioned separator in between and

$\text{Ni}_{0.70}\text{Mn}_{0.20}\text{Al}_{0.10}(\text{OH})_2$ ,  $\text{Ni}_{0.50}\text{Mn}_{0.40}\text{Al}_{0.10}(\text{OH})_2$ , in which a portion of the nickel element in the nickel hydroxide was replaced with element manganese and the element aluminum.

[0023] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.85}\text{Mn}_{0.05}\text{Al}_{0.10}\text{O}_2$  (Working Example 8 [sic]),  $\text{LiNi}_{0.70}\text{Mn}_{0.20}\text{Al}_{0.10}\text{O}_2$  (Working Example 9 [sic]), and  $\text{LiNi}_{0.50}\text{Mn}_{0.40}\text{Al}_{0.10}\text{O}_2$  (Working Example 10 [sic]) was performed.

[0024] (4) Working examples 10 to 12

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 65:5:30, 60:10:30 and 50:20:30 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas  $\text{Ni}_{0.65}\text{Mn}_{0.05}\text{Al}_{0.30}(\text{OH})_2$ ,  $\text{Ni}_{0.60}\text{Mn}_{0.10}\text{Al}_{0.30}(\text{OH})_2$ , and  $\text{Ni}_{0.50}\text{Mn}_{0.20}\text{Al}_{0.30}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0025] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas  $\text{LiNi}_{0.65}\text{Mn}_{0.05}\text{Al}_{0.30}\text{O}_2$  (Working Example 10),  $\text{LiNi}_{0.60}\text{Mn}_{0.10}\text{Al}_{0.30}\text{O}_2$  (Working Example 11), and  $\text{LiNi}_{0.50}\text{Mn}_{0.20}\text{Al}_{0.30}\text{O}_2$  (Working Example 12) was performed.



[0026] (5) Working examples 13 to 15

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 55:5:40, 50:10:40 and 50:5:45 were prepared.

Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas

$\text{Ni}_{0.55}\text{Mn}_{0.05}\text{Al}_{0.40}(\text{OH})_2$ ,  $\text{Ni}_{0.50}\text{Mn}_{0.10}\text{Al}_{0.40}(\text{OH})_2$ , and  $\text{Ni}_{0.50}\text{Mn}_{0.05}\text{Al}_{0.45}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0027] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas  $\text{LiNi}_{0.55}\text{Mn}_{0.05}\text{Al}_{0.40}\text{O}_2$  (Working Example 13),  $\text{LiNi}_{0.50}\text{Mn}_{0.10}\text{Al}_{0.40}\text{O}_2$  (Working Example 14), and  $\text{LiNi}_{0.50}\text{Mn}_{0.05}\text{Al}_{0.45}\text{O}_2$  (Working Example 15) was performed.

[0028] Each positive electrode active material of Working Example 1 to Working Example 15 produced as described above was arranged for the powder X-ray analyzer and when measurements were made for each positive electrode active material as Cu-K $\alpha$  X-rays were applied at a radiation angle of theta using the Cu-K $\alpha$  X-ray source and a slit with a slit width of 1  $\mu\text{m}$  and measurement was performed for the half-band width of the peaks existing in the range of  $2\theta=18.71\pm0.25$  degrees, the results shown in Table I below were obtained. Furthermore, when measurements were made of the intensity of the peaks observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peaks observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, the results shown in Table I below were obtained.

[0029]

[Table I]

Type of positive electrode active material	Molar ratio of each element				b+c	Half-band width (°)	Intensity ratio of peak
	Li	Ni	Mn	Al			
Work. Ex. 1	1.00	0.95	0.05	0.00	0.05	0.16	1.8
Work. Ex. 2	1.00	0.70	0.30	0.00	0.30	0.20	1.5
Work. Ex. 3	1.00	0.55	0.45	0.00	0.45	0.22	1.7
Work. Ex. 4	1.00	0.90	0.05	0.05	0.10	0.18	1.3
Work. Ex. 5	1.00	0.65	0.30	0.05	0.35	0.20	1.1
Work. Ex. 6	1.00	0.50	0.45	0.05	0.50	0.19	1.3
Work. Ex. 7	1.00	0.85	0.05	0.10	0.15	0.17	1.5
Work. Ex. 8	1.00	0.70	0.20	0.10	0.30	0.18	1.5
Work. Ex. 9	1.00	0.50	0.40	0.10	0.50	0.20	1.9
Work. Ex. 10	1.00	0.65	0.05	0.30	0.35	0.20	1.7
Work. Ex. 11	1.00	0.60	0.10	0.30	0.40	0.17	1.8
Work. Ex. 12	1.00	0.50	0.20	0.30	0.50	0.18	1.5
Work. Ex. 13	1.00	0.55	0.05	0.40	0.45	0.22	1.7
Work. Ex. 14	1.00	0.50	0.10	0.40	0.50	0.21	1.1
Work. Ex. 15	1.00	0.50	0.05	0.45	0.50	0.21	1.2

[0030] In the Table I above, the relative amount of Li is a in the composition formula

$\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$ , Ni is  $1-(b+c)$ , Mn is b, and Al (when M is Al) is c. As is clearly shown in the above-mentioned Table I, the composite oxides of each working example of 1 to 15 where the half-band width of the peak of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when measurement is done by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source satisfies all the conditions of  $0<a\leq1.2$ ,  $0.05\leq b\leq0.45$ ,  $0\leq c\leq0.45$  and  $0.05<b+c\leq0.50$ , that is,  $0.5\leq1-(b+c)\leq0.95$ .

## [0031] (6) Comparative Example 1

First, the nickel sulfate solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned solution as stirring was being performed and an adjustment was made for the pH of the solution. In this manner, production of nickel hydroxide was achieved. Subsequently, mixing was performed for nickel hydroxide and lithium hydroxide in such a manner that the molar ratio of the lithium and nickel of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in composition formula  $\text{LiNiO}_2$  (Comparative Example 1) was achieved.

## [0032] (7) Comparative Example 2

First, a mixed solution, in which the molar ratio of the nickel in a nickel sulfate solution and the molar ratio of the manganese in a manganese sulfate solution were adjusted to 50:50 was prepared. Then, the above-mentioned mixed solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned mixed solution as stirring was being performed and an adjustment was made for the pH of the mixed solution. In this manner, production of a nickel-manganese hydroxide, in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese as shown in the composition formulas  $\text{Ni}_{0.50}\text{Mn}_{0.50}(\text{OH})_2$  was achieved.

[0033] Subsequently, mixing was performed for the above-mentioned nickel-manganese composite oxide and a lithium hydroxide ( $\text{LiOH}$ ) in such a manner that a molar ratio of the lithium and nickel-manganese of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in composition formula  $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$  (Comparative Example 2) was achieved.

Example 1),  $\text{LiNi}_{0.70}\text{Mn}_{0.30}\text{O}_2$  (Working Example 2), and  $\text{LiNi}_{0.55}\text{Mn}_{0.45}\text{O}_2$  (Working Example 3) was performed.

[0020] (2) Working Examples 4 to 6

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 90:5:5, 65:30:5 and 50:45:5 were prepared.

Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned Working Examples 1 to 3 so as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the structural formulas of

$\text{Ni}_{0.90}\text{Mn}_{0.05}\text{Al}_{0.05}(\text{OH})_2$ ,  $\text{Ni}_{0.65}\text{Mn}_{0.35}\text{Al}_{0.05}(\text{OH})_2$ , and  $\text{Ni}_{0.05}\text{Mn}_{0.45}\text{Al}_{0.05}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0021] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 and mixing was performed; then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas  $\text{LiNi}_{0.90}\text{Mn}_{0.05}\text{Al}_{0.05}\text{O}_2$  (Working Example 4),  $\text{LiNi}_{0.65}\text{Mn}_{0.30}\text{Al}_{0.05}\text{O}_2$  (Working Example 5), and  $\text{LiNi}_{0.50}\text{Mn}_{0.45}\text{Al}_{0.05}\text{O}_2$  (Working Example 6) was performed.

[0022] (3) Working Examples 7 to 9

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 85:5:10, 70:20:10 and 50:40:10 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas  $\text{Ni}_{0.85}\text{Mn}_{0.05}\text{Al}_{0.10}(\text{OH})_2$ ,

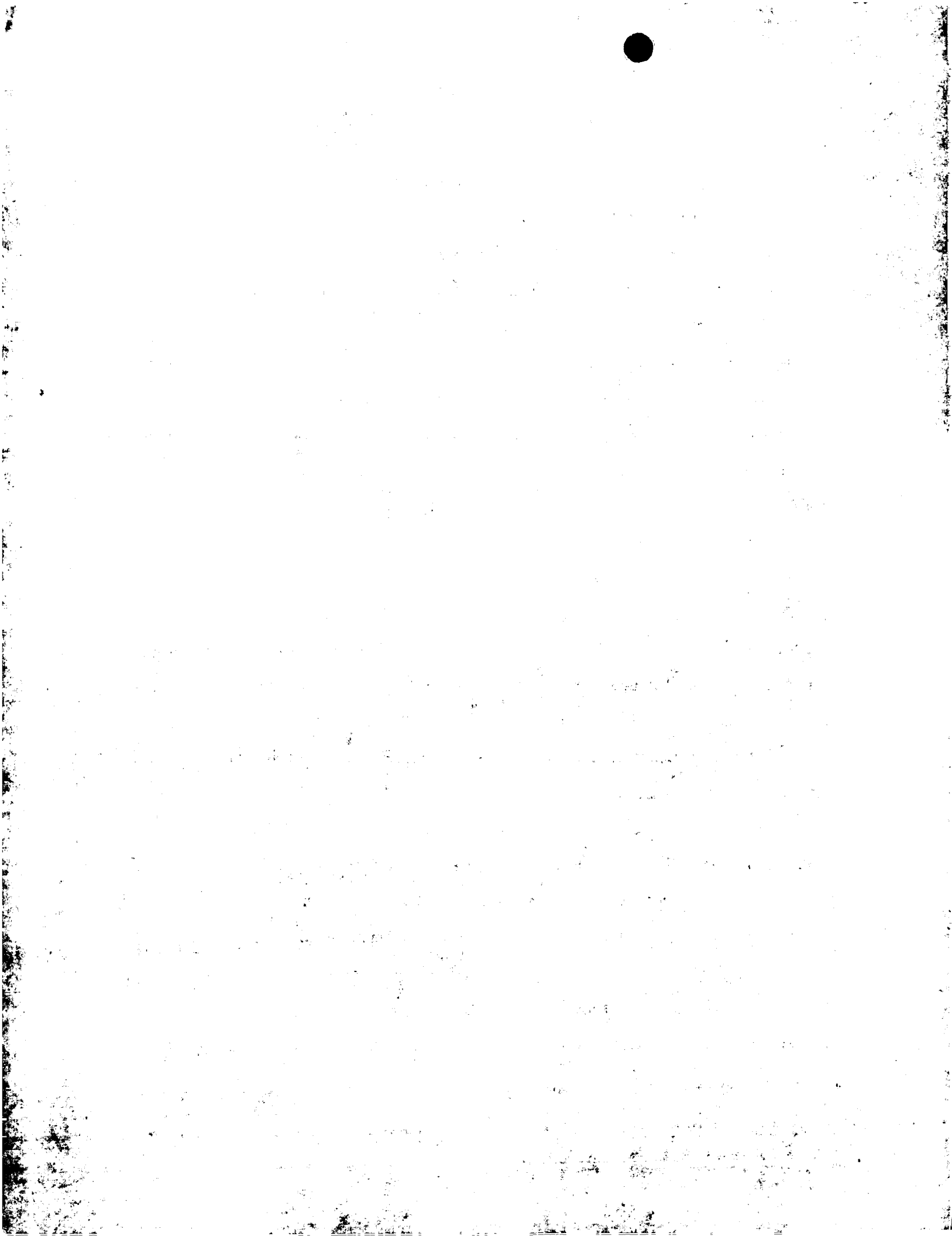
general, an increase in the half-band width of the peak of the powder X-ray analysis occurs when a dissimilar element is non-uniformly mixed with a given substance, and a non-uniform solid solubility of cobalt element and manganese element is suggested since the half-band width of the peak of the powder X-ray analysis of the lithium-nickel-cobalt-manganese composite oxide produced by the method proposed in the above-mentioned Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007 is higher than the half-band width of the case where an element other than nickel is included.

[0007]

[Means to solve the problem and work of invention] Based on the above-mentioned background, the present invention is to eliminate the above-mentioned existing problems, and the purpose of the present invention is to produce a positive electrode active material with a reinforced crystal structure of lithium-nickel composite oxide so as to produce a positive electrode for lithium secondary battery and a lithium secondary battery with improved cycle characteristics and load characteristics.

[0008] Thus, the positive electrode active material for lithium secondary battery is provided with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.45$  and  $0.5 \leq 1-(b+c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source.

[0009] Furthermore, the positive electrode active material for lithium secondary battery is provided with a lithium-nickel-manganese-M composite oxide shown in structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.40$



being lightweight and small in size, and a lithium secondary battery that utilizes lithium-cobalt composite oxide ( $\text{LiCoO}_2$ ) as the positive electrode material is used in practice.

[0003] However, lithium secondary batteries that utilize a lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) as the positive electrode material is not used in practice. As a reason, inadequate cycle characteristics of lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) based on disturbance of the crystal structure of the material can be mentioned. In addition, due to brittle crystal structure, the material cannot withstand the sudden storing and releasing of lithium ion at a high charge-discharge rates.

[0004] Thus, a method, in which a portion of the nickel element of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is replaced with a different element so as to reinforce the crystal structure and to improve the cycle characteristics is being examined. For example, a method, in which a portion of the nickel element of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is substituted with the element cobalt and the element manganese to stabilize the crystal structure, and a manganese compound containing trivalent or higher manganese is used so that formation of an inert  $\text{Li}_2\text{MnO}_3$  or a rock salt made of  $\text{NiO}$  is electrochemically controlled is proposed in Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007.

[0005]

[Problems to be solved by the invention] However, the effect achieved by the method proposed in Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007 is still inadequate. In the method proposed in the above-mentioned publication, an improvement in cycle characteristics is observed when a heat-treatment is performed for a lithium compound, nickel compound, cobalt compound, and manganese compound in comparison to the case where a portion of the nickel element is replaced with a cobalt element and manganese element but without forming into a composite, but the effect achieved is still inadequate.

[0006] In this case, distribution of the substituted cobalt element and manganese element is non-uniform, and the reinforcement effect on the crystal structure is inadequate. It is known that in

loaded into a battery tube and a nonaqueous solution is filled inside the aforementioned battery tube.

[Claim 29] The method of manufacturing lithium secondary battery described in claim 27 or claim 28 characterized by the fact that the coprecipitation process, in which the pH of the mixed solution of a solution of a dissolved nickel compound and a solution of a dissolved manganese compound or a mixed solution of a solution of a dissolved nickel compound, a solution of a dissolved manganese compound and a solution of dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 30] The method of manufacturing a lithium secondary battery described in claim 27 or claim 28 characterized by the fact that the evaporation drying process, in which evaporation drying is performed for the mixed solution comprising a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution comprising a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising a fine particles of each of the aforementioned compounds, is included.

[Claim 31] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 30, in which a heat-treatment process where a mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.



above-mentioned composite oxide, a positive electrode active material with improved cycle characteristics and load characteristics can be produced. Therefore, the cycle characteristics and load characteristics of the positive electrode that utilizes the active material made of the above-mentioned composite oxide are improved and furthermore, the cycle characteristics and load characteristics of the lithium secondary battery that utilizes the above-mentioned positive electrode are improved as well.

[0013] Furthermore, when a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is uniformly replaced with Mn or Mn and another element M, and the ratio of the intensity of the peak observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, is below 0.8, formation of impurities such as  $\text{Li}_2\text{Ni}_8\text{O}_{10}$  are conceivable. In this case, the impurities have an adverse effect on crystal structure, which leads to problems such as reduction in capacity; thus, it is desirable for the value of the intensity ratio, I1/I2, to be at least 0.8.

[0014] In a conventional synthesis method where mixing is performed for the raw material powders and baking is done is used in production of a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is uniformly replaced with Mn or Mn and another element M, it is difficult to uniformly replace a portion of the nickel element in the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) with Mn or Mn and other element M, as a result, the value of the half-band width measured by the powder X-ray analysis is increased, and the degree of improvement in the cycle characteristics and load characteristics is insufficient.

[0015] Therefore, in the method of manufacturing the positive electrode active material of the present invention, uniform replacement of a portion of the nickel element of lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide is required. For example, a coprecipitation process, in which the

pH of a mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution comprising a solution with a dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is required.

[0016] As a different example, an evaporation drying process, in which evaporation drying is performed for the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is required. Furthermore, when a heat-treatment is performed for a mixture of the composite hydroxide produced in the above-mentioned process (coprecipitation process, or evaporation drying process) and a mixture of lithium compound under an oxygen atmosphere, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel in the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is uniformly replaced with Mn or Mn and another element M, can be produced.

[0017] When the above-mentioned coprecipitation process, or evaporation drying process is provided, it is possible to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) is uniformly replaced with Mn or Mn and another element M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti). In the above-mentioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, the crystal structure is adequately reinforced, and

a positive electrode active material with improved cycle characteristics and load characteristics can be produced. Therefore, the cycle characteristics and load characteristics of the positive electrode that utilize the above-mentioned active material made of the above-mentioned composite oxide are improved and furthermore, the cycle characteristics and load characteristics of the lithium secondary battery that utilizes the above-mentioned positive electrode are improved as well.

[0018]

[Embodiment of the invention] Suitable embodiments of the present invention are explained in detail below.

#### 1. Production of positive electrode active material

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution and the molar ratio of manganese in manganese sulfate solution of 95:5, 90:30 and 55:45 were prepared. Each of the above-mentioned mixed solutions was poured into a stirring tank and sodium hydroxide solution was slowly added as stirring was performed in the stirring tank and an adjustment was made to the pH of the mixed solutions. As a result of the above-mentioned stirring, three different types of nickel-manganese composite hydroxide given by the composition formulas  $\text{LiNi}_{0.95}\text{Mn}_{0.05}(\text{OH})_2$ ,  $\text{Ni}_{0.70}\text{Mn}_{0.30}(\text{OH})_2$ ,  $\text{Ni}_{0.55}\text{Mn}_{0.45}(\text{OH})_2$ , in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese were produced.

[0019] Subsequently, an adjustment was made for the above-mentioned nickel-manganese hydroxides and lithium hydroxide ( $\text{LiOH}$ ) so as to form a molar ratio of the lithium and nickel-manganese of 1:1 and mixing was performed, then, a heat-treatment was performed at a temperature of  $750^\circ\text{C}$  for 20 hours under an oxygen atmosphere to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of positive electrode active materials made of three different types of lithium-nickel-manganese composite oxides shown in structural formulas  $\text{LiNi}_{0.95}\text{Mn}_{0.05}\text{O}_2$  (Working

[Claim 32] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 31, in which the M in the aforementioned structural formula is Al.

[Claim 33] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 32, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having a ratio of the intensity of the peak observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peak observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, upon measurement by the aforementioned powder X-ray analysis of at least 0.8 is formed.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention pertains to a positive electrode active material capable of electrochemically storing and releasing lithium, and the invention further pertains to a positive electrode for lithium secondary battery with an improved cycle characteristics and load characteristics and manufacturing method of same, positive electrode for lithium secondary battery made of the positive electrode active material and manufacturing method of same, and lithium secondary battery made of the positive electrode and manufacturing method of same.

[0002]

[Prior art] In recent years, lithium secondary batteries represented by lithium ion batteries comprising a negative active material that utilizes a carbon material capable of storing and releasing the aforementioned lithium metal, lithium alloy or lithium ion and a positive electrode material a lithium-containing transition metal composite oxide such as lithium-cobalt composite material ( $\text{LiCoO}_2$ ), lithium-nickel composite material ( $\text{LiNiO}_2$ ) and lithium-manganese composite material ( $\text{LiMn}_2\text{O}_4$ ) are used as a battery for portable electronics and communication machines such as small video cameras, cell phones and notebook computers since high discharge voltage that matches the 4V class, high energy density and high capacity can be achieved despite

The nickel sulfate solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned solution as stirring was being performed and an adjustment was made for the pH of the solution. In this manner, production of nickel hydroxide was performed. Subsequently, mixing was performed for nickel hydroxide and lithium hydroxide in such a manner that the molar ratio of the lithium and nickel of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in structural formulas  $\text{LiNiO}_2$  (comparative example 1) was achieved.

[0034] (8) Comparative examples 3 and 4

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 92:3:5 and 45:50:5. Then, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas  $\text{Ni}_{0.92}\text{Mn}_{0.03}\text{Al}_{0.05}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.50}\text{Al}_{0.05}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0035] Subsequently, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 was achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.92}\text{Mn}_{0.03}\text{Al}_{0.05}\text{O}_2$  (Comparative Example 3) and  $\text{LiNi}_{0.45}\text{Mn}_{0.50}\text{Al}_{0.05}\text{O}_2$  (Comparative Example 4).

[0036] (9) Comparative Example 5

First, a mixed solution, in which the molar ratio of the nickel in a nickel sulfate solution and the molar ratio of the aluminum in an aluminum sulfate solution were adjusted to form 90:10. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce a nickel-aluminum composite hydroxide shown in the composition formula  $\text{Ni}_{0.90}\text{Al}_{0.10}(\text{OH})_2$ , in which a portion of the nickel element in the nickel hydroxide was replaced with the element aluminum. Subsequently, mixing was performed for the above-mentioned nickel-aluminum with lithium in such a manner that a molar ratio of the lithium and nickel-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce a positive electrode active material comprising the lithium-nickel-aluminum composite oxide shown in the composition formula  $\text{LiNi}_{0.90}\text{Al}_{0.10}\text{O}_2$  (Comparative example 5).

[0037] (10) Comparative Examples 6 and 7

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 87:3:10 and 45:45:10. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas  $\text{Ni}_{0.87}\text{Mn}_{0.03}\text{Al}_{0.10}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.45}\text{Al}_{0.10}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was substituted with a manganese element and an aluminum element.

[0038] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite hydroxides with lithium in such a manner that a molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of working examples 1 to 3 so as to produce two different types of positive electrode active materials comprised of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.87}\text{Mn}_{0.03}\text{Al}_{0.10}\text{O}_2$

(Comparative Example 6) and  $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Al}_{0.10}\text{O}_2$  (Comparative Example 7).

[0039] (11) Comparative Examples 8 and 9

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to form 67:3:30 and 45:25:30. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 above so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas of and

$\text{Ni}_{0.67}\text{Mn}_{0.03}\text{Al}_{0.30}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.25}\text{Al}_{0.30}(\text{OH})_2$ , in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0040] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprised of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.67}\text{Mn}_{0.03}\text{Al}_{0.30}\text{O}_2$  (Comparative Example 8) and  $\text{LiNi}_{0.45}\text{Mn}_{0.25}\text{Al}_{0.30}\text{O}_2$  (Comparative Example 9).

[0041] (12) Comparative Examples 10 and 11

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to form 57:3:40 and 45:15:40. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas  $\text{Ni}_{0.57}\text{Mn}_{0.03}\text{Al}_{0.40}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.15}\text{Al}_{0.40}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0042] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.57}\text{Mn}_{0.03}\text{Al}_{0.40}\text{O}_2$  (Comparative Example 10) and  $\text{LiNi}_{0.45}\text{Mn}_{0.15}\text{Al}_{0.40}\text{O}_2$  (Comparative Example 11).

[0043] (13) Comparative Examples 12 and 13

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 52:3:45 and 45:10:45. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 above so as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the structural formulas of  $\text{Ni}_{0.52}\text{Mn}_{0.03}\text{Al}_{0.45}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.10}\text{Al}_{0.45}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0044] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising the lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.52}\text{Mn}_{0.03}\text{Al}_{0.45}\text{O}_2$  (Comparative Example 12) and  $\text{LiNi}_{0.45}\text{Mn}_{0.10}\text{Al}_{0.45}\text{O}_2$  (Comparative Example 13).

[0045] (14) Comparative Examples 14 and 15

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and



the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 47:3:50 and 45:5:50. Then, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas of  $\text{Ni}_{0.47}\text{Mn}_{0.03}\text{Al}_{0.50}(\text{OH})_2$  and  $\text{Ni}_{0.45}\text{Mn}_{0.05}\text{Al}_{0.50}(\text{OH})_2$  in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0046] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.47}\text{Mn}_{0.03}\text{Al}_{0.50}\text{O}_2$  (Comparative Example 14) and  $\text{LiNi}_{0.45}\text{Mn}_{0.05}\text{Al}_{0.50}\text{O}_2$  (Comparative Example 15).

[0047] (15) Comparative Examples 16 to 21

An adjustment was made in such a manner that the following molar ratios of each of the elements Li, Ni, Mn and Al in lithium hydroxide ( $\text{LiOH}$ ), nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ ) and manganese dioxide ( $\text{MnO}_2$ ) to form 100:90:10:0, 100:70:20:0, 100:50:40:10, 100:50:20:30, 100:40:20:40 were produced. After mixing was performed for the above-mentioned materials in a mortar, a heat-treatment and pulverization were performed as in the case Working Examples 1 to 3 above so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-composite oxides and four different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas  $\text{LiNi}_{0.90}\text{Mn}_{0.10}\text{O}_2$  (Comparative example 16),  $\text{LiNi}_{0.70}\text{Mn}_{0.30}\text{O}_2$  (Comparative Example 17),  $\text{LiNi}_{0.70}\text{Mn}_{0.20}\text{Al}_{0.10}\text{O}_2$  (Comparative Example 18),  $\text{LiNi}_{0.50}\text{Mn}_{0.40}\text{Al}_{0.10}\text{O}_2$  (Comparative Example 19),  $\text{LiNi}_{0.50}\text{Mn}_{0.20}\text{Al}_{0.30}\text{O}_2$  (Comparative Example 20), and  $\text{LiNi}_{0.40}\text{Mn}_{0.20}\text{Al}_{0.40}\text{O}_2$  (Comparative Example 21).

[0048] Each positive electrode active material of the above-mentioned Comparative Example 1 to Comparative Example 21 produced as described above was arranged for the powder X-ray analyzer and when a measurement was performed for each positive electrode active material as Cu-K $\alpha$  rays were applied at a radiation angle of theta using the Cu-K $\alpha$  X-ray source and a slit with a slit width of 1  $\mu$ m and measurements were made of the half-band width of the peaks existing in the range of  $2\theta=18.71\pm0.25$  degrees, and the results shown in Table II below were obtained. Furthermore, when a measurement was performed for the intensity of the peaks observed at  $2\theta=18.71\pm0.25$  degrees (I1) and the intensity of the peaks observed at  $2\theta=44.54\pm0.25$  degrees (I2), I1/I2, the results shown in Table II below were obtained.

[0049]

[Table II]

Type of positive electrode active material	Molar ratio of each element				b+c	Half-band width (°)	Intensity ratio of peak
	Li	Ni	Mn	Al			
Comp. Ex. 1	1.00	1.00	0.00	0.00	0.00	0.17	1.9
Comp. Ex. 2	1.00	0.50	0.50	0.00	0.50	0.21	1.2
Comp. Ex. 3	1.00	0.92	0.03	0.05	0.08	0.20	1.2
Comp. Ex. 4	1.00	0.45	0.50	0.05	0.55	0.21	1.7
Comp. Ex. 5	1.00	0.90	0.00	0.10	0.10	0.17	1.8
Comp. Ex. 6	1.00	0.87	0.03	0.10	0.13	0.17	1.8
Comp. Ex. 7	1.00	0.45	0.45	0.10	0.55	0.19	1.7
Comp. Ex. 8	1.00	0.67	0.03	0.30	0.33	0.21	1.9
Comp. Ex. 9	1.00	0.45	0.25	0.30	0.55	0.20	1.6
Comp. Ex. 10	1.00	0.57	0.03	0.40	0.43	0.17	1.7
Comp. Ex. 11	1.00	0.45	0.15	0.40	0.55	0.20	1.7
Comp. Ex. 12	1.00	0.52	0.03	0.45	0.48	0.19	1.7
Comp. Ex. 13	1.00	0.45	0.10	0.45	0.55	0.19	1.6
Comp. Ex. 14	1.00	0.47	0.03	0.50	0.53	0.18	1.5
Comp. Ex. 15	1.00	0.45	0.05	0.50	0.55	0.20	1.7
Comp. Ex. 16	1.00	0.90	0.10	0.00	0.10	0.27	1.7
Comp. Ex. 17	1.00	0.70	0.30	0.00	0.30	0.25	1.8
Comp. Ex. 18	1.00	0.70	0.20	0.10	0.30	0.31	1.2
Comp. Ex. 19	1.00	0.50	0.40	0.10	0.50	0.29	1.1
Comp. Ex. 20	1.00	0.50	0.20	0.30	0.50	0.30	1.6
Comp. Ex. 21	1.00	0.40	0.20	0.40	0.60	0.27	1.4

[0050] In Table II above, Li is a in the structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$ , Ni is  $1-(b+c)$ , Mn is b, and Al (when M is Al) is c. As is clearly shown in Table II above, the composite oxides of

each Comparative Examples 1 through 15 where the half-band width of the peak of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) observed at  $2\theta=18.71\pm0.25$  degrees is not in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where  $\text{Cu-K}\alpha$  beam is used as the X-ray source, in other words, the conditions  $0<a<1.2$ ,  $0.05\leq b\leq 0.45$ ,  $0\leq c\leq 0.45$  and  $0.05<b+c<0.50$ , that is,  $0.5\leq 1-(b+c)\leq 0.95$ , is not met.

[0051] 2. Production of composite oxide positive electrode

Mixing was performed for 90 parts by weight of each of positive electrode active material produced in the above-mentioned Working Examples 1 to 15 and Comparative Examples 1 to 21, 5 parts by weight of synthetic graphite, and N-methyl-2-pyrrolidone (NMP) solution of 5 parts by weight polyvinylidene fluoride and production was performed for positive electrode active material slurries of Working Examples 1 to 15 and positive electrode active material slurries of Comparative Examples 1 to 21. Each of the above-mentioned positive electrode active material slurries was coated onto the both surfaces of a positive electrode current collector made of an aluminum foil using the doctor blade method to form a positive electrode active material layer; then, vacuum drying was performed for 2 hours at  $150^\circ\text{C}$  and production of positive electrode of Working Examples 1 to 15 and positive electrode of Comparative Examples 1 to 21 was achieved.

[0052] 3. Production of negative electrode

Mixing was performed for 95 parts by weight of a negative electrode material capable of achieving intercalation and deintercalation of lithium ion (for example, natural graphite) and an N-methyl-2-pyrrolidone (NMP) solution of 5 parts by weight polyvinylidene fluoride to produce a negative electrode slurry. The resulting negative electrode slurry was coated onto both surfaces of a negative electrode current collector made of copper foil using the doctor blade method to form a negative electrode active material layer, then, vacuum drying was performed for 2 hours at  $150^\circ\text{C}$  and production of negative electrode was performed. For the negative electrode active material used in this case, a carbon type material capable of achieving intercalation and

deintercalation of lithium ion, for example, graphite, carbon black, coke, glassy carbon, carbon fiber, and baked materials of the same can be used effectively. Furthermore, an oxide capable of achieving intercalation and deintercalation of lithium ion such as tin oxide or titanium oxide can be used in this case as well.

[0053] 4. Production of lithium secondary battery

The lead is attached to the positive electrode plate produced in the above-mentioned working examples 1 to 15 of the present invention and comparative examples 1 to 21, and the lead is attached to the negative electrode plate produced as described above, and the above-mentioned positive electrode plates and negative electrode plates are wrapped in a coil with a separator in between so as to form a coiled electrode.

[0054] Each of the above-mentioned coiled electrodes is loaded into a battery case (AA size, for example), and the leads are connected to the positive terminal and negative terminal, respectively. Then, an electrolyte solution produced by adding 1 mole/liter of lithium phosphate hexafluoride ( $\text{LiPF}_6$ ) to an equal volume mixture solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) was injected to the above-mentioned case, and it was sealed to produce the sample batteries of Working Examples 1 to 15 of the present invention and Comparative Examples 1 to 21 with a rated flow capacity of 580 mA·h. In this case, the shape of the above-mentioned batteries is not limited, and flat, square, or cylinder-form may be used.

[0055] In this case, in addition to the above-mentioned mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), a mixture of an aprotic solvent without capacity of feeding a hydrogen ion and dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), etc. may be used as well. Furthermore, in addition to the above-mentioned  $\text{LiPF}_6$ , imide salts represented by  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ , etc. may be used as electrolytes.

[0056] 5. Test

(1) Charge-discharge cycle test

Each battery produced in the above-mentioned Working Examples 1 to 15 and Comparative

Examples 1 to 21 were charged at room temperature (25°C) under 200 mA at a constant current to form 4.2 V, then, discharged under 200 mA at a constant current to form 2.75 V, and the above-mentioned charge-discharge cycle was repeatedly performed. And the number of cycles until the discharge capacity became 90% or less of the initial discharge capacity was obtained. The results obtained are shown in Table III below (Batteries of Working Examples 1 to 15) and Table IV below (batteries of Comparative Examples 1 to 21).

[0057] (2) Load characteristic test

Each battery produced in the above-mentioned Working Examples 1 to 15 and Comparative Examples 1 to 21 was charged at room temperature (25°C) under 200 mA at a constant current to 4.2 V, then, discharged under 200 mA at a constant current to 2.75 V, and charge capacity (AmAh) was obtained. Meanwhile, charging was performed at room temperature (25°C) under 200 mA at a constant current to 4.2 V, then, discharged under 400 mA at a constant current to 2.75 V, and discharge capacity (BmAh) was obtained. The discharge capacity ratio B/A was calculated as the load characteristic, and the results obtained are shown in Table III below (Batteries of Working Examples 1 to 15) and Table IV below (batteries of Comparative Examples 1 to 21).

[0058]

[Table III]

Type of positive electrode active material	Half-band width (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Work. Ex. 1	0.16	1.8	120	0.90
Work. Ex. 2	0.20	1.5	129	0.91
Work. Ex. 3	0.22	1.7	119	0.92
Work. Ex. 4	0.18	1.3	172	0.96
Work. Ex. 5	0.20	1.1	170	0.97
Work. Ex. 6	0.19	1.3	179	0.96
Work. Ex. 7	0.17	1.5	176	0.98
Work. Ex. 8	0.18	1.5	173	0.97
Work. Ex. 9	0.20	1.9	169	0.96
Work. Ex. 10	0.20	1.7	175	0.97
Work. Ex. 11	0.17	1.8	174	0.95
Work. Ex. 12	0.18	1.5	168	0.96
Work. Ex. 13	0.22	1.7	181	0.97
Work. Ex. 14	0.21	1.1	178	0.97
Work. Ex. 15	0.21	1.2	125	0.91

[0059]

[Table IV]

Type of positive electrode active material	Half-band width (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Comp. Ex. 1	0.17	1.9	13	0.75
Comp. Ex. 2	0.21	1.2	53	0.78
Comp. Ex. 3	0.20	1.2	67	0.82
Comp. Ex. 4	0.21	1.7	71	0.85
Comp. Ex. 5	0.17	1.8	69	0.84
Comp. Ex. 6	0.17	1.8	75	0.82
Comp. Ex. 7	0.19	1.7	79	0.85
Comp. Ex. 8	0.21	1.9	67	0.81
Comp. Ex. 9	0.20	1.6	58	0.83
Comp. Ex. 10	0.17	1.7	60	0.82
Comp. Ex. 11	0.20	1.7	59	0.86
Comp. Ex. 12	0.19	1.7	62	0.84
Comp. Ex. 13	0.19	1.6	67	0.85
Comp. Ex. 14	0.18	1.5	59	0.80
Comp. Ex. 15	0.20	1.7	60	0.81
Comp. Ex. 16	0.27	1.7	52	0.75
Comp. Ex. 17	0.25	1.8	54	0.72
Comp. Ex. 18	0.31	1.2	57	0.76
Comp. Ex. 19	0.29	1.1	52	0.79
Comp. Ex. 20	0.30	1.6	51	0.77
Comp. Ex. 21	0.27	1.4	49	0.79

[0060] As clearly shown in the results in Table III and Table IV, superior cycle characteristics and load characteristics were achieved in the composite oxides in each of Working Examples 1



to 15 shown in the composition formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$  where the half-band width of the peak of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source and satisfies all the following conditions:  $0<a<1.2$ ,  $0.05\leq b\leq 0.45$ ,  $0\leq c\leq 0.45$  and  $0.05<b+c<0.50$ , that is,  $0.5\leq 1-(b+c)\leq 0.95$ , in comparison to composite oxide of Comparative Examples 1 to 21, where one of the above-mentioned conditions is not satisfied.

[0061] In this case, it is hypothesized that good results are achieved as a result of the reinforced crystal structure achieved through uniform replacement of a portion of the Ni in Li-Ni composite oxide with Mn or Mn and Al. Furthermore, when a comparison is made among composite oxides of Working Examples 1 to 3 and Working Example 15 and composite oxide of Working Examples 4 to 14, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 4 to 14 is used. In this case, it is hypothesized that the good results are achieved as a result of an increase in uniformity in Ni, Mn and Al based on an approximate degree of formation of composite between Ni and the element other than Mn (Al).

[0062] 6. Examination of element added (Working Examples 16 to 25)

In the above-mentioned examples, the case where a part of the Ni in Li-Ni composite oxide is replaced with Mn or Mn and Al is used, and a further examination was performed with elements other than Al. In this case, nickel sulfate, manganese sulfate and compounds listed in Table V below were used as raw materials in production of composite oxides and production was performed as in the case where aluminum sulfate was used and production of composite oxides of Working Examples 16 to 25 was performed.

[0063]

[Table V]

Type of positive electrode active material	Raw material other than nickel sulfate and manganese sulfate	Composition of composite hydroxide	Half-band width (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Work. Ex. 16	H <sub>3</sub> BO <sub>4</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> B <sub>0.2</sub> (OH) <sub>2</sub>	0.20	1.2	159	0.94
Work. Ex. 17	FeSO <sub>4</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Fe <sub>0.1</sub> (OH) <sub>2</sub>	0.19	1.4	153	0.93
Work. Ex. 18	VO SO <sub>4</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> V <sub>0.1</sub> (OH) <sub>2</sub>	0.17	1.5	151	0.95
Work. Ex. 19	CrSO <sub>4</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Cr <sub>0.1</sub> (OH) <sub>2</sub>	0.20	1.2	160	0.92
Work. Ex. 20	CuSO <sub>4</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Cu <sub>0.1</sub> (OH) <sub>2</sub>	0.18	1.1	158	0.93
Work. Ex. 21	Ga <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Ga <sub>0.1</sub> (OH) <sub>2</sub>	0.20	1.2	157	0.92
Work. Ex. 22	Ca(NO <sub>3</sub> ) <sub>2</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Ca <sub>0.1</sub> (OH) <sub>2</sub>	0.18	1.5	151	0.93
Work. Ex. 23	Mg(NO <sub>3</sub> ) <sub>2</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Mg <sub>0.1</sub> (OH) <sub>2</sub>	0.20	1.4	149	0.95
Work. Ex. 24	Sr(NO <sub>3</sub> ) <sub>2</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Sr <sub>0.1</sub> (OH) <sub>2</sub>	0.19	1.2	160	0.93
Work. Ex. 25	Ti(SO <sub>4</sub> ) <sub>2</sub>	Ni <sub>0.7</sub> Mn <sub>0.2</sub> Ti <sub>0.1</sub> (OH) <sub>2</sub>	0.21	1.3	153	0.94

\* Translator's note: illegible - best guess

[0064] Subsequently, with each of the composite oxides produced in the above-mentioned Working Examples 16 to 25, production of composite oxide positive electrodes was performed, and furthermore, production of batteries of Working Examples 16 to 25 with a rated flow capacity of 580 mA·h was performed with the above-mentioned negative electrode and separator as described above. For each battery produced above, the charge-discharge cycle test and load characteristics test were performed as described above, and the results obtained are shown in Table V.

[0065] As shown in the results of the above-mentioned Table V, each of the composite oxide of Working Examples 16 to 25 satisfies the half-band width of the peak of the lithium-nickel composite oxide (LiNiO<sub>2</sub>) observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to

0.22 degrees when measurement is performed by the powder X-ray analysis where Cu-K $\alpha$  beam is used as the X-ray source satisfying all the following conditions:  $0 < a < 1.2$ ,  $0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.45$  and  $0.05 < b+c < 0.50$ , that is,  $0.5 \leq 1-(b+c) \leq 0.95$ .

[0066] Furthermore, when a comparison is made among composite oxides of Comparative Examples 1 to 21 shown in Table IV and composite oxides of the above-mentioned Working Examples 16 to 25 shown in Table V, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 16 to 25 is used. As shown in the results obtained above, as an element other than Al, elements selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti can be used effectively as well. Furthermore, when a comparison is made among composite oxides of Working Examples 8 and Working Examples 16 to 25, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 8 is used. In this case, higher uniformity is achieved with Al in comparison to that of Ni and Mn.

[0067] 7. Examination of peak ratio

In production of the above-mentioned composite oxides of Working Examples 1 to 15 and composite oxides of Working Examples 16 to 25, a heat-treatment was performed for 20 hours in an oxygen atmosphere at a temperature of 750°C, and the change in the peak based on the above-mentioned baking temperature was examined.

[0068] (1) Working Examples 26 to 28

A heat-treatment was performed for a mixture of the composite hydroxide of Working Example 8 and lithium hydroxide for 20 hours under an oxygen atmosphere at a temperature of 800°C (composite oxide of Working Example 26), a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 850°C (composite oxide of Working Example 27), and a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 900°C (composite oxide of Working Example 28).

[0069] (2) Working Examples 29 to 31

A heat-treatment was performed for a mixture of the composite hydroxide of Working Example 24 and lithium hydroxide for 20 hours under an oxygen atmosphere at a temperature of 770°C (composite oxide of Working Example 29), a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 790°C (composite oxide of Working Example 30), and a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 810°C (composite oxide of Working Example 31).

[0070] Subsequently, with each of the composite oxide produced in the above-mentioned Working Examples 26 to 31, production of composite oxide positive electrode was performed as described above, and furthermore, production of batteries of Working Examples 26 to 31 with a rated flow capacity of 580 mAH was performed with the above-mentioned negative electrode and separator as described above. For each battery produced above, the charge-discharge cycle test and load characteristics test were performed as described above, and the results obtained are shown in Table VI.

[0071]

[Table VI]

Type of positive electrode active material	Baking temperature (°C)	Half-band with (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Work. Ex. 26	800	0.18	1.2	170	0.96
Work. Ex. 27	850	0.19	0.8	172	0.95
Work. Ex. 28	900	0.17	0.5	159	0.92
Work. Ex. 29	770	0.20	1.0	157	0.93
Work. Ex. 30	790	0.21	0.8	169	0.92
Work. Ex. 31	810	0.19	0.7	145	0.90

[0072] When comparison is made among composite oxide of Working Example 8 and composite oxides of Working Examples 26, 27, 29 and 30 having the peak intensity ratio of 0.8 or higher and composite oxides of Working Examples 28 and 31 having the peak intensity ratio of 0.8 or below, a reduction in cycle characteristics and load characteristics is observed even among composite oxides having the half-band width of the peak of the lithium-nickel composite oxide ( $\text{LiNiO}_2$ ) observed at  $2\theta=18.71\pm0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source satisfy all the following conditions:  $0<a<1.2$ ,  $0.05\leq b\leq0.45$ ,  $0\leq c\leq0.45$  and  $0.05<b+c<0.50$ , that is,  $0.5\leq 1-(b+c)\leq0.95$ . In this case, impurities such as  $\text{Li}_2\text{Ni}_8\text{O}_{10}$  are formed when the peak intensity ratio is 0.8 or below and the crystal structure is adversely influenced; thus, it is desirable to use a composite oxide having a value of the intensity ratio of at least 0.8.

[0073] As described above, the crystal structure is reinforced in the lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in the structural formula  $\text{Li}_a\text{Mn}_b\text{M}_c\text{Ni}_{1-(b+c)}\text{O}_2$ , (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time,  $0<a<1.2$ ,

$0.05 \leq b \leq 0.45$ ,  $0 \leq c \leq 0.40$  and  $0.5 \leq 1 - (b + c) \leq 0.95$ ) and having the half-band width of the peak observed at  $2\theta = 18.71 \pm 0.25$  degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-K $\alpha$  beam is used as the X-ray source. Thus, the cycle characteristics and load characteristics of positive electrodes made of the above-mentioned active material can be improved, and furthermore, the cycle characteristics and load characteristics of the lithium secondary batteries made of the above-mentioned active material can be improved.

[0074] In the above-mentioned embodiments, first, the coprecipitation process, in which stirring is performed for a mixed solution of nickel sulfate and manganese sulfate, or nickel sulfate, manganese sulfate and an aluminum sulfate (In this case, instead of an aluminum sulfate, a compound containing B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, or Ti may be used, as well) so as to change the pH of the mixed solution and precipitation of the composite hydroxide is performed, then, a heat-treatment is further performed for the above-mentioned composite hydroxide produced and lithium hydroxide to produce the composite oxide. But the present invention is not limited to the above-mentioned embodiments, for example, the evaporation drying process can be used as well, in which evaporation drying is performed for the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution consisting of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, and a heat-treatment is performed for the above-mentioned composite raw material and lithium hydroxide to produce a composite oxide.